

Generalization of Gibbs Entropy and Thermodynamic Relation

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Abstract

In this paper, we extend the Gibbs's approach of quasi-equilibrium thermodynamic process, and show that, in general non-equilibrium thermodynamic process, the microscopic expression of entropy is given as

$$S(t) = - \int dx \rho(x, t) \ln \int dx' \rho(x', t) \phi_{\Delta t}(x, x', t),$$

where $\rho(x, t)$ is the ensemble distribution in phase space and $\phi_{\Delta t}(x, x', t)$ is the probability density to obtain that, in macroscopic observation, the system with initial value x' in phase space at time t is found at state x after time collapse $\frac{\Delta t}{2}$, and Δt is the maximum value of the time interval for which any macroscopic thermodynamic variables increase linearly. Also, we analyze the formal structure of thermodynamic relation in non-equilibrium thermodynamic process.

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Since Gibbs had found the microscopic expression of entropy in the course of analyzing the quasi-equilibrium thermodynamic process [1, 2], there have been much effort to formulate the generalized theory for entropy to be applicable in non-equilibrium thermodynamic process. Although recent progress related with the fluctuation theorem gives some information necessary to obtain such generalization [3–6], it seems still far from obtaining adequate foundation for the general theory of entropy, in that we have not yet gained a clear connection between entropy and microdynamics in non-equilibrium process. The purpose of this paper is to develop a consistent theory to connect entropy and the classical dynamics in general non-equilibrium process. Especially, it shall be shown that the developed theory overcomes the conventional problem as the Gibbs entropy cannot discriminate the irreversible variation of a closed Hamiltonian dynamical system as it is an invariant for such system (by Liouville’s theorem), which is important in constructing systematic theory of arbitrary non-equilibrium thermodynamic process in future. In this work, we obtain the microscopic expression of entropy in general non-equilibrium thermodynamic process, and prove the entropy theorem for an arbitrary closed (ergodic and chaotic) Hamiltonian dynamical system. Also, we will obtain the extended thermodynamic relation for general thermodynamic process and derive the fluctuation theorem.

I. COMPLEX DYNAMICAL SYSTEM INTERACTING WITH EXTERNAL ENVIRONMENT

Let us consider the Hamiltonian system

$$\mathcal{H} = H(q, p) + V_{\text{int}}(q, \pi), \quad (1)$$

where the Hamiltonian system H defined by the coordinates $q \equiv (q_1, q_2, \dots, q_N)$ and momentum $p \equiv (p_1, p_2, \dots, p_N)$ interacts with its environment system, which is described by the coordinate $\pi \equiv (\pi_1, \pi_2, \dots, \pi_\nu)$, by the interaction potential $V_{\text{int}}(q, \pi)$. If there is macroscopic slow motion of π denoted by the time series $a(t) \equiv (a_1(t), a_2(t), \dots, a_\nu(t))$, we define new variable as $\pi'_i = \pi_i - a_i(t)$. In macroscopic point of view, the interaction by $a_i(t)$ is still interpreted as a mechanical interaction; on the contrary, the interaction by π'_i is the quantity interpreted as thermal interaction. Instead of using the variables π'_i , we replace the dynamical dependence of π'_i by the dependence of time t , as treat π'_i as a fast fluctuating

time series, and Hamiltonian is written as

$$\mathcal{H} = H(x) + V_{\text{int}}(q, a, t), \quad (2)$$

where $x \equiv (x_1, x_2, \dots, x_{2N}) \equiv (q_1, \dots, q_N, p_1, \dots, p_N) \equiv (q, p)$. Then, the probability density function (PDF) $\rho(x, t)$ describing the ensemble distribution in the phase space Γ defined by x satisfies the Liouville's equation:

$$\frac{\partial \rho(x, t)}{\partial t} = -iL(x, a, t)\rho(x, t), \quad (3)$$

where $iL(x, a, t) \equiv \sum_k \frac{\partial \mathcal{H}}{\partial p_k} \frac{\partial}{\partial q_k} - \sum_k \frac{\partial \mathcal{H}}{\partial q_k} \frac{\partial}{\partial p_k}$, and, by the normalization condition for $\rho(x, t)$,

$$\int \rho(x, t) dx = 1, \quad (4)$$

where $dx \equiv dx_1 dx_2 \dots dx_{2N}$.

Let the characteristic time interval for our macroscopic measurement system be Δt in the sense that the error ξ_0 of macroscopic time-measurement is given within the error range

$$-\frac{\Delta t}{2} < \xi_0 < \frac{\Delta t}{2} \quad (5)$$

approximately. In such case, *the experimentally discriminable minimum of time collapse from a given instant is $\frac{\Delta t}{2}$ in statistical sense*. Then, the time series $a_i(t)$ can be interpreted as a time-averaged behavior of $\pi_i(t)$ during the error range Δt such as $\frac{1}{\Delta t} \int_t^{t+\Delta t} \pi_i(t') dt'$, and we reasonably request that, if there is increment $\Delta a \equiv (\Delta a_1, \Delta a_2, \dots, \Delta a_\nu)$ in a during Δt , Δa_i is a linear function of Δt :

$$\Delta a_i \propto \Delta t. \quad (6)$$

Generally, since arbitrary macroscopic slow variation in system \mathcal{H} can be interpreted as such a time-averaged behavior of some complex dynamical variation during Δt , *Δt is the maximum time interval during which we can approximate any macroscopic thermodynamic variable varies linearly for time*.

On the other hand, based on the dynamic complexity of system \mathcal{H} , for the experimentally discriminable minimum time collapse $\frac{\Delta t}{2}$, we have the following presupposition: since we assume that, including the case where the system is completely isolated from the external variation as $\pi_i = \text{const}$, there are always some fast chaotic and ergodic motions such that their trajectory vary non-linearly during $\frac{\Delta t}{2}$, we have

$$\hat{T} e^{-i \int_t^{t+\frac{\Delta t}{2}} L(x, \tau) d\tau} \not\approx 1 - iL(x, a, t) \frac{\Delta t}{2}, \quad (7)$$

where $L(x, \tau) \equiv L(x, a(\tau), \tau)$ and \hat{T} denotes the time-ordering operator which interchanges the operators to follow in chronological order from right to left; if the system is completely isolated, it is written as $e^{-iL(x, a)\frac{\Delta t}{2}} \approx 1 - iL(x, a)\frac{\Delta t}{2}$.

Similarly, if the characteristic interval of x for the given macroscopic measurement system is $\Delta x \equiv (\Delta x_1, \Delta x_2, \dots, \Delta x_{2N})$ in the sense that the error $\xi \equiv (\xi_1, \xi_2, \dots, \xi_{2N})$ of the macroscopic measurement for $x \equiv (x_1, x_2, \dots, x_{2N})$ satisfies the error range

$$-\frac{\Delta x_i}{2} < \xi_i < \frac{\Delta x_i}{2} \quad (8)$$

approximately, we assume that, including the case of the completely isolated system, there are always some complex (chaotic and ergodic) motions macroscopically undescrivable as a smooth path in the sense that, by these complex motions, the velocity field in Γ or the Liouville operator $L(x, a, t)$ cannot be approximated linearly for the increment $\frac{\Delta x_i}{2}$ in x ; thus we have

$$L(x_i + \frac{\Delta x_i}{2}, a, t) \not\approx L(x, a, t) + \frac{\partial L(x, a, t)}{\partial x_i} \frac{\Delta x_i}{2}. \quad (9)$$

In the followings, we will trace the rational consequence of the presupposition (5), (6), (7), (8), and (9).

II. MACROSCOPIC BEHAVIOR OF ENSEMBLE DISTRIBUTION

For the macroscopic system characterizing such value Δt and Δx , the experimentally observed quantity for $\rho(x, t)$ is given by $\tilde{\rho}(x, t)$ as

$$\tilde{\rho}(x, t) = \frac{1}{\Delta t \Delta \Gamma} \int_t^{t+\Delta t} \int_x^{x+\Delta x} dt' dx' \rho(x', t'), \quad (10)$$

where $\Delta \Gamma$ is the volume of Δx ; or more precisely

$$\tilde{\rho}(x, t) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} d\xi_0 d\xi f(\xi, \xi_0) \rho(x + \xi, t + \xi_0), \quad (11)$$

where $f(\xi, \xi_0)$ is the PDF to obtain the errors ξ and ξ_0 . The slow varying property of $\tilde{\rho}(x, t)$ can be expressed as

$$\tilde{\rho}(x, t + \Delta t) \approx \tilde{\rho}(x, t) + \frac{\partial \tilde{\rho}(x, t)}{\partial t} \Delta t, \quad (12a)$$

$$\tilde{\rho}(x_i + \Delta x_i, t) \approx \tilde{\rho}(x, t) + \frac{\partial \tilde{\rho}(x, t)}{\partial x_i} \Delta x_i, \quad (12b)$$

and, by the normalization condition for $\tilde{\rho}(x, t)$,

$$\int \tilde{\rho}(x, t) dx = 1. \quad (13)$$

The slow varying property of $\tilde{\rho}(x, t)$ means that, for a given thermodynamic process, $\tilde{\rho}(x, t)$ is expressible by a smaller set of independent physical observables $\epsilon \equiv (\epsilon_1, \epsilon_2, \dots, \epsilon_{\mathcal{N}})$ than x , where ϵ_i is defined by x and a , i.e., $\epsilon = \epsilon(x, a)$; for example, the energy $H(x) + V_{\text{int}}(q, a)$ in (1) can be one of the such observables.¹ Although the number and kind of the observables ϵ_i alters depending on the concerned thermodynamic process, we expect generally $\mathcal{N} \ll N$ for the conventional thermodynamic system with Avogadro's number of degrees of freedom. Finally, more specifically, we write the expression of $\tilde{\rho}(x, t)$ as

$$\tilde{\rho}(x, t) = \tilde{\rho}(\epsilon(x, a), t); \quad (14)$$

in abbreviation, we will use the notation $\tilde{\rho}(\epsilon(x, a), t) \equiv \tilde{\rho}(\epsilon, t)$.² Corresponding to the variation of the external parameter a , the statistical properties of each dynamical variables ϵ_i are expected to vary slowly. Thus, we assume that we can control the statistical properties of ϵ_i with appropriate time series $a(t)$ and the external thermal environment.

Using the cumulants [7], we can write as

$$\tilde{\rho}(\epsilon(x, a), t) = \text{const} \cdot \int_{-\infty}^{\infty} \exp \left[-ik \cdot x + \sum_{|m|=1}^{\infty} \frac{K_m}{m!} (ik)^m \right] dk, \quad (16)$$

where $k \equiv (k_1, k_2, \dots, k_{2N})$ and $k \cdot x \equiv \sum_i k_i x_i$, and $m \equiv (m_1, m_2, \dots, m_{2N})$ is multi-index; the cumulants K_m is given as

$$K_m(a, t) = (-i)^{|m|} \left[\frac{\partial^{|m|}}{\partial k^m} \ln \sum_{|l|=0}^{\infty} \frac{\langle x^l \rangle}{l!} (ik)^l \right]_{k=0} \quad (17)$$

with multi-index $l = (l_1, l_2, \dots, l_{2N})$ and the notation $\langle x^l \rangle \equiv \int \tilde{\rho}(x, t) x^l dx$. Thus, we write $\tilde{\rho}(\epsilon, t)$ as a function of K_m : $\tilde{\rho}(\epsilon, t) = \tilde{\rho}(\epsilon, K_m)$. Because K_m varies slowly as $a_i(t)$, we have

$$K_m(a + \Delta a, t + \Delta t) \approx K_m(a, t) + \frac{dK_m(a, t)}{dt} \Delta t. \quad (18)$$

¹ More precisely, ϵ_i should be defined by x and π , but macroscopically the value of $\epsilon_i(x, \pi)$ for a state x comes from the time average for $\pi(t)$ during Δt , and only the linearly increasing component $a(t)$ in $\pi(t)$ is effective, as $\pi'(t)$ is a fast fluctuating time series.

² With the expression (14) and (6), the condition (12a) can be rewritten as

$$\tilde{\rho}(\epsilon(x, a + \Delta a), t + \Delta t) \approx \tilde{\rho}(\epsilon(x, a), t) + \sum_{i,j} \frac{\partial \tilde{\rho}(\epsilon(x, a), t)}{\partial \epsilon_i} \frac{\partial \epsilon_i}{\partial a_j} \Delta a_j + \frac{\partial \tilde{\rho}(\epsilon(x, a), t)}{\partial t} \Delta t. \quad (15)$$

With multi-index $n = (n_1, n_2, \dots, n_{\mathcal{N}})$, let us define c_n as

$$\tilde{\rho}(x, t) = \tilde{\rho}(\epsilon, K_m) = e^{\sum_{|n|=0}^{\infty} c_n \epsilon^n}, \quad (19)$$

i.e.,

$$c_n(a, t) = \left[\frac{1}{n!} \frac{\partial^{|n|}}{\partial \epsilon^n} \ln \tilde{\rho}(\epsilon, K_m) \right]_{\epsilon=0}. \quad (20)$$

Then, considering (18), c_n varies slowly also as

$$\Delta c_n = c_n(a + \Delta a, t + \Delta t) - c_n(a, t) \approx \frac{dc_n}{dt} \Delta t. \quad (21)$$

Finally we write $\tilde{\rho}(\epsilon, t)$ as a function of c_n :

$$\tilde{\rho}(\epsilon(x, a), t) = \tilde{\rho}(\epsilon(x, a), c_n). \quad (22)$$

III. EXPRESSION OF ENTROPY AND PROOF OF THE ENTROPY THEOREM

Now, after time Δt from t , we have ensemble distribution $\tilde{\rho}(\epsilon(x, a + \Delta a), c_n + \Delta c_n)$. Applying (6), (12), (21), and the normalization condition (13), we have

$$\begin{aligned} & \int (e^{\ln \tilde{\rho}(\epsilon(x, a + \Delta a), c_n + \Delta c_n)} - e^{\ln \tilde{\rho}(\epsilon(x, a), c_n)}) dx \\ &= \int \tilde{\rho} \left(\sum_{|n|=0}^{\infty} \frac{\partial \ln \tilde{\rho}}{\partial c_n} \Delta c_n + \sum_{i,j} \frac{\partial \ln \tilde{\rho}}{\partial \epsilon_j} \frac{\partial \epsilon_j}{\partial a_i} \Delta a_i \right) dx \\ &= 0, \end{aligned} \quad (23)$$

where $\tilde{\rho} \equiv \tilde{\rho}(\epsilon, c_n)$. Using (19) and $\sum_j \partial_{\epsilon_j} \ln \tilde{\rho} \cdot \partial_{a_i} \epsilon_j = \sum_{|n|=1}^{\infty} c_n \partial_{a_i} \epsilon^n$, and noting that, since the averaged quantities

$$\langle \epsilon^n \rangle \equiv \int \tilde{\rho}(x, t) \epsilon^n dx \quad (24)$$

vary slowly as (12), we have $\langle \epsilon^n \rangle \Delta c_n = \Delta(\langle \epsilon^n \rangle c_n) - c_n \Delta \langle \epsilon^n \rangle$, we obtain

$$\sum_{|n|=1}^{\infty} c_n \Delta \langle \epsilon^n \rangle - \sum_{|n|=1}^{\infty} \sum_i c_n \frac{\partial \langle \epsilon^n \rangle}{\partial a_i} \Delta a_i - \Delta \left(\sum_{|n|=0}^{\infty} c_n \langle \epsilon^n \rangle \right) = 0. \quad (25)$$

Comparing with the approach for the quasi-equilibrium process given by Gibbs and Einstein [1, 2], it can be understood that the first and second term respectively correspond to the terms describing the energy variation and the work performed on external system in the equilibrium thermodynamics, and the third term corresponds to the variation of the Gibbs entropy.

Let us denote the third term in (25) as

$$\bar{S}(t) \equiv - \sum_{|n|=0}^{\infty} c_n \langle \epsilon^n \rangle = - \int \tilde{\rho}(x, t) \ln \tilde{\rho}(x, t) dx. \quad (26)$$

Using the simplified notation as $\int_t^{t+\Delta t} dt' \int_x^{x+\Delta x} dx' \dots \equiv \int_{t,x,\dots}^{\Delta} dt' dx' \dots$,³ and by the condition (12) for the slow varying property of $\tilde{\rho}(x, t)$, in zeroth order of Δt , we can write as

$$\begin{aligned} \bar{S}(t) &= - \frac{1}{\Delta t \Delta \Gamma} \int dx \int_{t,x}^{\Delta} dt' dx' \rho(x', t') \ln \tilde{\rho}(x', t') \\ &= - \frac{1}{\Delta t} \int_t^{\Delta} dt' \int dx \rho(x, t') \ln \frac{1}{\Delta t \Delta \Gamma} \int_{t',x}^{\Delta} ds dy \rho(y, s). \end{aligned} \quad (28)$$

Here, from the Liouville's equation (3), $\rho(y, s)$ in the last integral can be expressed as

$$\begin{aligned} \rho(y, s) &= \hat{T} [e^{-i \int_{t'}^s L(y, \tau) d\tau}] \rho(y, t') \\ &= \int dy' \rho(y', t') \hat{T} [e^{-i \int_{t'}^s L(y, \tau) d\tau}] \delta(y - y'). \end{aligned} \quad (29)$$

Thus, finally we obtain

$$\begin{aligned} \bar{S}(t) &= - \frac{1}{\Delta t} \int_t^{\Delta} dt' \int dx \rho(x, t') \ln \int dy' \rho(y', t') \\ &\quad \times \frac{1}{\Delta t \Delta \Gamma} \int_{t',x}^{\Delta} ds dy \hat{T} [e^{-i \int_{t'}^s L(y, \tau) d\tau}] \delta(y - y'). \end{aligned} \quad (30)$$

And correspondingly the microdynamical expression for entropy, S should be given as

$$S(t) = - \int dx \rho(x, t) \ln \int dx' \rho(x', t) \frac{1}{\Delta t \Delta \Gamma} \int_{t,x}^{\Delta} ds dy \hat{T} [e^{-i \int_t^s L(y, \tau) d\tau}] \delta(y - x'). \quad (31)$$

In above expression (31), we have to note that, considering the error range $-\frac{\Delta t}{2} < \xi_0 < \frac{\Delta t}{2}$, the last integral term express the probability density $p_{\Delta t}(x|x', t)$ to occur (in macroscopic realm) the event that the system initially positioned at x' in Γ at t is found at position x after time collapse $\frac{\Delta t}{2}$, i.e.,

$$p_{\Delta t}(x|x', t) = \frac{1}{\Delta t \Delta \Gamma} \int_{t,x}^{\Delta} ds dy \hat{T} [e^{-i \int_t^s L(y, \tau) d\tau}] \delta(y - x') \quad (32)$$

³ As a special case of this notation, we will use $\int_x^{\Delta} dx' \equiv \int_x^{x+\Delta x} dx'$ and $\int_t^{\Delta} dt' \equiv \int_t^{t+\Delta t} dt'$.

⁴ In obtaining the second line of (28), we have used

$$\int dx \rho(x, t) \dots = \int dx \frac{1}{\Delta \Gamma} \int_x^{\Delta} dx' \rho(x', t) \dots \quad (27)$$

and it is the quantity describing the irreversible variation of the dynamical system initially positioned at x' .⁵ Because of the fast chaotic and ergodic motions generating the result (7) and (9), $p_{\Delta t}(x|x', t)$ is different from δ -function, as the range of x over which $p_{\Delta t}(x|x', t) \neq 0$ cannot be covered by Δx , and the irreversibility contained in the Louville operator $L(x, a, t)$ exactly corresponds to this irreversible functional variation from the initial distribution $\delta(x - x')$. As the initial position x' is changed, $p_{\Delta t}(x|x', t)$ gives the complete information of the irreversibility of entire dynamics at t . In the following analysis, with the given above entropy expression, we will prove the entropy theorem for the completely isolated system.

Let us consider the completely isolated system as $\pi_i = \text{const.}$ Then $p_{\Delta t}(x|x', t)$ is independent of t :

$$p_{\Delta t}(x|x') = \frac{1}{\Delta t \Delta \Gamma} \int_{0,x}^{\Delta} ds dy e^{-iL(y)s} \delta(y - x'). \quad (34)$$

For the fast chaotic and ergodic motions in the completely isolated system, we request that these complex motions make the following statement established:

$p_{\Delta t}(x|x')$ is a slow varying function for x and x' as $\tilde{\rho}$ in the sense of (12).

Then, by the above slow varying condition for $p_{\Delta t}(x|x')$ and using

$$e^{-iL(y)s} \delta(y - x) = e^{iL(x)s} \delta(y - x), \quad (35)$$

we can write the followings:

$$\begin{aligned} p_{\Delta t}(x|x') &= \frac{1}{\Delta t \Delta \Gamma} \int_{x,0}^{\Delta} dy ds e^{-iL(y)s} \delta(y - x') \\ &= \frac{1}{\Delta t \Delta \Gamma^2} \int_{x',x,0}^{\Delta} dy' dy ds e^{-iL(y)s} \delta(y - y') \\ &= \frac{1}{\Delta t \Delta \Gamma^2} \int_{x,x',0}^{\Delta} dy dy' ds e^{iL(y')s} \delta(y - y') \\ &= \frac{1}{\Delta t \Delta \Gamma^2} \int_{x,x',0}^{\Delta} dy dy' ds e^{-iL(y')(s-\Delta t)} \delta(y - y') \\ &= \frac{1}{\Delta t \Delta \Gamma^2} \int_{x,x',0}^{\Delta} dy dy' ds e^{-iL(y')s - iL(y)\Delta t} \delta(y - y') \\ &= \frac{1}{\Delta \Gamma} \int_x^{\Delta} dy e^{-iL(y)\Delta t} p_{\Delta t}(x'|y). \end{aligned} \quad (36)$$

⁵ If we use the more precise definition (11) for $\tilde{\rho}$, the expression (32) is replaced by

$$p_{\Delta t}(x|x', t) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} d\xi_0 d\xi f(\xi, \xi_0) \hat{T} \left[e^{-i \int_{t-\frac{\Delta t}{2}}^{t+\frac{\xi_0}{2}} L(x+\xi, \tau) d\tau} \right] \delta(x + \xi - x'). \quad (33)$$

On the other hand, from (10) and (29), $\tilde{\rho}(x, t)$ can be written as

$$\tilde{\rho}(x, t) = \int dx' \rho(x', t) p_{\Delta t}(x|x'), \quad (37)$$

from which, using $\rho(x', t - \Delta t) = e^{iL(x')\Delta t} \rho(x', t)$ and the Hermitian property of operator $L(x')$, we obtain

$$\tilde{\rho}(x, t - \Delta t) - \tilde{\rho}(x, t) = \int dx' \rho(x', t) (e^{-iL(x')\Delta t} - 1) p_{\Delta t}(x|x') \quad (38)$$

and similarly, using Liouville's equation (3),

$$\frac{\partial \tilde{\rho}(x, t)}{\partial t} = \int dx' \rho(x', t) iL(x') p_{\Delta t}(x|x'). \quad (39)$$

With δ -function $\delta(x) \equiv \delta(x_1)\delta(x_2) \cdots \delta(x_{2N})$, let us define the macroscopic δ -function $\tilde{\delta}(x)$ as

$$\tilde{\delta}(x) \equiv \frac{1}{\Delta \Gamma} \int_x^\Delta \delta(\Delta x - y) dy. \quad (40)$$

Then, substituting (38) and (39) to condition (12), and replacing $\rho(x', t)$ by $\tilde{\delta}(x' - y')$ with the notion that (38) and (39) hold for arbitrary $\rho(x', t)$, it follows that

$$\frac{1}{\Delta \Gamma} \int_{y'}^\Delta dx' e^{-iL(x')\Delta t} p_{\Delta t}(x|x') \approx p_{\Delta t}(x|y') - \Delta t \cdot \frac{i}{\Delta \Gamma} \int_{y'}^\Delta dx' L(x') p_{\Delta t}(x|x'), \quad (41)$$

for the description of $\tilde{\rho}(x, t)$ as conditioned by (12). Finally from (36) and the approximation (41), we have the following result in macroscopic realm:

$$p_{\Delta t}(x|x') = p_{\Delta t}(x'|x). \quad (42)$$

Also, since $\tilde{\rho}(x, t)$ is expressed as in (37) for the completely isolated system, integrating both sides of (37) by $\frac{1}{\Delta t} \int_t^\Delta dt'$ and using the relation given from the condition (12)

$$\begin{aligned} \frac{1}{\Delta t} \int_t^\Delta dt' \tilde{\rho}(x, t') &\approx \frac{1}{\Delta t} \int_t^\Delta dt' [\tilde{\rho}(x, t) + \partial_t \tilde{\rho}(x, t) \cdot (t' - t)] \\ &\approx \tilde{\rho}(x, t + \frac{\Delta t}{2}) \end{aligned} \quad (43)$$

and the formula (27), we have

$$\begin{aligned} \tilde{\rho}(x, t + \frac{\Delta t}{2}) &= \frac{1}{\Delta t} \int_t^\Delta dt' \int dx' \rho(x', t') p_{\Delta t}(x|x') \\ &= \int dx' \frac{1}{\Delta t \Delta \Gamma} \int_{t, x'}^\Delta dt' dy \rho(y, t') p_{\Delta t}(x|y) \\ &= \int dx' \tilde{\rho}(x', t) p_{\Delta t}(x|x'), \end{aligned} \quad (44)$$

because $p_{\Delta t}(x|x')$ is a slow varying function for x and x' as $\tilde{\rho}$. And, with (44) and (12), we obtain the result

$$\frac{\partial \tilde{\rho}(x, t)}{\partial t} = \frac{2}{\Delta t} \int dx' p_{\Delta t}(x|x') [\tilde{\rho}(x', t) - \tilde{\rho}(x, t)], \quad (45)$$

where we have used $\int dx' p_{\Delta t}(x|x') = \int dx' p_{\Delta t}(x'|x) = 1$.

Thus, from the definition (26) and (45),

$$\frac{d\bar{S}(t)}{dt} = -\frac{2}{\Delta t} \int dx \int dx' p_{\Delta t}(x|x') [\tilde{\rho}(x', t) - \tilde{\rho}(x, t)] [1 + \ln \tilde{\rho}(x, t)]. \quad (46)$$

Exchanging x and x' , we obtain a different expression of $\frac{d\bar{S}(t)}{dt}$, and, adding these two expressions and using (42),

$$\frac{d\bar{S}(t)}{dt} = -\frac{1}{\Delta t} \int dx \int dx' p_{\Delta t}(x|x') [\tilde{\rho}(x', t) - \tilde{\rho}(x, t)] \ln \frac{\tilde{\rho}(x, t)}{\tilde{\rho}(x', t)}. \quad (47)$$

Because $p_{\Delta t}(x|x')$ given by (34) cannot be a δ -function in macroscopic realm as is defined in (40), and the equilibrium state of the completely isolated system is identified as $\tilde{\rho}(x, t) = \text{const}$ on an appropriate energy surface, we have

$$\frac{d\bar{S}(t)}{dt} > 0, \quad (48)$$

if the system is in non-equilibrium state as $\tilde{\rho}(x, t) \neq \text{const}$ on the energy surface; for the equilibrium state, $\frac{d\bar{S}(t)}{dt} = 0$.

Consequently, as is manifested in comparison with the process of derivation of the Boltzmann transport equation [8, 9], the term $p_{\Delta t}(x|x')$ makes the role corresponding to the scattering matrix in the Boltzmann transport equation. Similarly as the scattering matrix in Boltzmann's theory describes the effect of the local intermolecular interaction given by physical potential (such as Coulomb potential), the term $p_{\Delta t}(x|x')$ describes the effect of the fast chaotic and ergodic motions resulting (7) and (9). If we consider the systems initially positioned in the volume $(x, x + \Delta x)$ in Γ , while these initial conditions are macroscopically un-discriminable as the differences between them fall within the error range, the fast complex motions changes the each systems with the finely differentiated initial conditions to be respectively in completely different positions in Γ after time collapse Δt (or $\frac{\Delta t}{2}$). And macroscopically this dynamical process related with the fast complex motions can be understood as a $\frac{N}{3}$ -body scattering-like process. To gain more physically intuitive picture for the calculation process of the entropy theorem, we rewrite entropy \bar{S} given by (26), (30) and

(34) as follows using the relation (44) in zeroth order of Δt :

$$\bar{S}(t) = -\frac{1}{2} \int dx \int dx' \tilde{\rho}(x, t) V^\Gamma(x, x', t) \tilde{\rho}(x', t), \quad (49)$$

where

$$V^\Gamma(x, x', t) = p_{\Delta t}(x|x') \left[\frac{\ln \tilde{\rho}(x, t)}{\tilde{\rho}(x, t)} + \frac{\ln \tilde{\rho}(x', t)}{\tilde{\rho}(x', t)} \right]. \quad (50)$$

If we interpret $V^\Gamma(x, x', t)$ as a potential interacting between two ensemble elements respectively positioned at x and x' in Γ at time t , the entropy theorem (48) simply means that the ensemble system always behaves to decrease the total potential energy induced by the ensemble potential $V^\Gamma(x, x', t)$. And, since $p_{\Delta t}(x|x') \not\approx \tilde{\delta}(x - x')$ by the fast chaotic and ergodic motions resulting (7) and (9), it means that generally the elements of the ensemble interact with each other through the potential $V^\Gamma(x, x', t)$; since we can expect from definition (34) that $p_{\Delta t}(x|x')$ and $V^\Gamma(x, x', t)$ have the tendency to decrease as the distance $|x - x'|$ increases in Γ , we can say that the interaction by $V^\Gamma(x, x', t)$ is overall repulsive.⁶ In macroscopic observation realm, the fast chaotic and ergodic motions generating the results (7) and (9) emerges as a potential giving the interaction between the ensemble elements in phase space Γ ; especially, if the ensemble system is equilibrium ($\tilde{\rho} = \text{const}$ on an appropriate energy surface), the potential is given by $V^\Gamma(x, x', t) \propto p_{\Delta t}(x|x')$. We use the notation $\phi_{\Delta t}(x, x', t)$ instead of $p_{\Delta t}(x|x', t)$ to emphasize the meaning of $p_{\Delta t}(x|x', t)$ as a ensemble potential originated from dynamic correlation, and the microscopic expression of entropy is written as

$$S(t) = - \int dx \rho(x, t) \ln \int dx' \rho(x', t) \phi_{\Delta t}(x, x', t), \quad (51)$$

where $\phi_{\Delta t}(x, x', t) \equiv p_{\Delta t}(x|x', t)$ is given by the expression (32).

Finally, we point out that it is logically natural that the expression of entropy contains the parameter Δt which specifies the scale of the given measurement system, in that the entropy increment of a system is essentially related with the microdynamical components which cannot be described in deterministic way under the given measurement system: these fine dynamical information deterministically un-catchable by the given measurement system increase as the measuring scale Δt increases. Under the given measurement system, the

⁶ On the contrary, in the original Gibbs entropy expression, it is treated as each ensemble elements in Γ are completely independent of each other as the original expression is written as $-\int dx \rho(x, t) \ln \int dx' \rho(x', t) \delta(x - x')$, that is, $p_{\Delta t}(x|x') = \delta(x - x')$.

observer loses such fine dynamical information, and, only when there is the loss of the deterministic dynamical information by measurement imperfection, the entropy increment arises. For the perfect observer ($\Delta t = 0$ and $\Delta x = 0$), the entropy expression becomes exactly the Gibbs entropy, i.e., $\bar{S}(t) = - \int dx \rho(x, t) \ln \rho(x, t)$, and thus there is no increment of entropy: $\frac{d\bar{S}}{dt} = 0$ as \bar{S} is dynamically invariant.

IV. MEANING OF THE ENTROPY THEOREM IN PHASE SPACE DYNAMICS

From the Liouville's equation (3), we can obtain the description for the macroscopic ensemble distribution $\tilde{\rho}(x, t)$ in Γ . Integrating both sides of the Liouville's equation (3) by $\int_{t,x}^{\Delta} dt' dx'$ and noting the expression (29), we have the results as

$$\frac{\partial \tilde{\rho}(x, t)}{\partial t} = - \sum_i \frac{\partial}{\partial x_i} \tilde{\rho}(x, t) \tilde{v}_i(x, t), \quad (52)$$

where, for the completely isolated system, $\tilde{v}_i(x, t)$ is given as

$$\begin{aligned} \tilde{v}_i(x, t) &\equiv \frac{1}{\tilde{\rho}(x, t) \Delta t \Delta \Gamma} \int_{t,x}^{\Delta} dt' dx' \dot{x}_i(x') \rho(x', t') \\ &= \int dx' \tilde{v}_i^o(x, x') \frac{\rho(x', t)}{\tilde{\rho}(x, t)} \end{aligned} \quad (53)$$

with the definition

$$\tilde{v}_i^o(x, x') \equiv \frac{1}{\Delta t \Delta \Gamma} \int_{0,x}^{\Delta} ds dy \dot{x}_i(y) e^{-iL(y)s} \delta(y - x'), \quad (54)$$

where $\dot{x}(x) \equiv (\dot{x}_1(x), \dot{x}_2(x), \dots, \dot{x}_{2N}(x)) \equiv (\dot{q}(x), \dot{p}(x))$ denotes the velocity field in Γ given by the Hamilton's equations of motion for $\mathcal{H}(x)$, i.e.,

$$\dot{x}(x) = (\partial_{p_1} \mathcal{H}, \dots, \partial_{p_N} \mathcal{H}, -\partial_{q_1} \mathcal{H}, \dots, -\partial_{q_N} \mathcal{H}); \quad (55)$$

if we integrate both sides of (53) by $\int_t^{\Delta} dt'$ and note that \tilde{v}_i^o and \tilde{v}_i is a slow varying function as $\tilde{\rho}(x, t)$, then, with the formula (27) and similar process as in (43) and (44), in zeroth order of Δt , (53) can be rewritten as ⁷

$$\tilde{v}_i(x, t) = \int dx' \tilde{v}_i^o(x, x') \frac{\tilde{\rho}(x', t)}{\tilde{\rho}(x, t)}. \quad (56)$$

⁷ As is indicated by the expression (56), $\Delta \Gamma \cdot \tilde{v}_i^o(y, y)$ is the velocity field (at position y in Γ) observed for the ensemble of the systems which are prepared to be in state y under the macroscopic measurement, i.e., $\tilde{\rho}(x) = \tilde{\delta}(x - y)$. And, for the ensemble system prepared as $\tilde{\rho}(x) = \frac{1}{2} \tilde{\delta}(x - y) + \frac{1}{2} \tilde{\delta}(x - y')$, $\Delta \Gamma \cdot \tilde{v}_i^o(y, y')$ is the contribution to the velocity field at y by the ensemble elements positioned at y' .

That is, $\tilde{v}_i(x, t)$ is the velocity field (in Γ) observed in macroscopic point of view, and the averaged macroscopic motion in Γ is given as

$$\frac{dx_i}{dt} = \tilde{v}_i(x, t). \quad (57)$$

Then, by the definition of entropy (26) and (52), we have

$$\frac{d\bar{S}(t)}{dt} = \int \tilde{\rho}(x, t) \sum_i \frac{\partial \tilde{v}_i(x, t)}{\partial x_i} dx. \quad (58)$$

Thus, (48) means that, for the completely isolated system, the macroscopically observed motion of the ensemble in Γ is not incompressible any more: generally,

$$\sum_i \frac{\partial \tilde{v}_i(x, t)}{\partial x_i} \neq 0, \quad (59)$$

and, in macroscopic realm, the local volume in Γ averagely expands, if the system is in non-equilibrium state ($\tilde{\rho} \neq \text{const}$ on an energy surface). Finally, if we treat the combined system of \mathcal{H} and its environment system as a closed (i.e., completely isolated) Hamiltonian system, the entropy theorem can be restated as *averagely the local volume in the total phase space always expands, if the total system is in non-equilibrium state as the ensemble distribution is not constant on an appropriate energy surface.*

V. THERMODYNAMIC RELATION

Reminding the assumption that we can macroscopically control the statistical properties of ϵ_i in (14), let us consider the process where $a(t)$ and the external thermal environment are given as they induce only the change of energy value $E \equiv H(x) + V_{\text{int}}(q, a)$ of the system (1): for $\tilde{\rho}(E, \epsilon_2, \epsilon_3, \dots, t)$, we consider the variation of E only as $\epsilon_i = \text{const}$. Then, the result corresponding to (25) is simply obtained by replacing ϵ in (25) with E :

$$\Delta \bar{S} = \sum_{n=1}^{\infty} \frac{1}{T_n} \Delta \bar{E}^{(n)} + \sum_{n=1}^{\infty} \frac{1}{T_n} \sum_i \bar{F}_i^{(n)} \Delta a_i, \quad (60)$$

where we have used the notations as $\bar{E}^{(n)} \equiv \langle E^n \rangle$, $T_n \equiv -\frac{1}{c_n}$, and

$$\bar{F}_i^{(n)} \equiv -\frac{\partial \langle E^n \rangle}{\partial a_i}. \quad (61)$$

In non-equilibrium process, we have (60) as a relation directly corresponding to the thermodynamic relation in the equilibrium thermodynamics.

The formulation (60) means that, in general non-equilibrium thermodynamic process, in addition to the average energy $\bar{E}^{(1)}$, we should treat the each statistical properties $\bar{E}^{(n)} \equiv \langle E^n \rangle$ of E as *independent* macroscopic thermodynamic variables. Also, to describe the mechanical interaction with the external environment, we should treat the new $\bar{E}^{(n)}$ -corresponding forces $\bar{F}_i^{(n)}$ defined by (61) in addition to the conventional force $\bar{F}_i^{(1)} = -\frac{\partial \langle E \rangle}{\partial a_i}$. In this case, the thermal characteristic of the system is completely determined by the quantities T_n , which is given by the relation (60) as

$$\frac{1}{T_n} = \frac{\partial \bar{S}}{\partial \bar{E}^{(n)}}, \quad (62)$$

where $n = 1, 2, \dots$ (T_1 is the temperature in the equilibrium thermodynamics). Keeping the conventional understanding of temperature as a quantity to describe the thermal characteristic of a system in relation with its entropy and energy variation, (60) means that, in general non-equilibrium process, the thermal characteristic of a system is specified by many temperatures T_n . That is, generally the temperature of a non-equilibrium thermodynamic system should be defined not by a single scalar quantity but by an array of temperatures

$$\mathbf{T} \equiv (T_1, T_2, \dots, T_n, \dots), \quad (63)$$

where the each component T_n is the measure of how the entropy \bar{S} increases as the statistical property $\langle E^n \rangle$ increases.

Let Σ be the space defined by the ordered-tuple (\mathbf{T}, a) . Since the ensemble distribution $\tilde{\rho}(x, t)$ at an instant is completely determined by the ordered-tuple (\mathbf{T}, a) , arbitrary thermodynamic process for a given system can be described as a path in the space Σ . If a system interacting with a thermal reservoir transforms from equilibrium state (T_1, a) to equilibrium state (T'_1, a') ,⁸ the entropy increment of the system during the process is path-independent in the space Σ , because entropy \bar{S} defined by (26) is a function of (\mathbf{T}, a) as $\langle \epsilon^n \rangle$ is a function of (\mathbf{T}, a) ; if R and I respectively represents a reversible and irreversible path connecting state (T_1, a) to state (T'_1, a') in Σ , the entropy increment for the reversible path $\int_R d\bar{S}$ is the same as that for the irreversible path $\int_I d\bar{S}$. Thus, by (60), we have

$$\int_R \frac{dQ^{(1)}}{T_1} = \int_I \frac{dQ^{(1)}}{T_1} + \sum_{n=2}^{\infty} \int_I \frac{dQ^{(n)}}{T_n}, \quad (64)$$

⁸ The notation (T_1, a) is the abbreviation for the case that $\frac{1}{T_n} = 0$ for $n \geq 2$ in (\mathbf{T}, a) .

where

$$dQ^{(n)} \equiv d\bar{E}^{(n)} + \sum_i \bar{F}_i^{(n)} da_i. \quad (65)$$

Let the thermal reservoir be quasi-ideal in the sense that the ensemble PDF of the closed total system (containing the thermal reservoir) is always given by the form

$$\tilde{\rho}_{\text{tot}} = e^{c_0 - \frac{\mathcal{E}}{\mathcal{T}} - \sum_{n=1}^{\infty} \frac{\bar{E}^{(n)}}{\mathcal{T}_n}}, \quad (66)$$

where \mathcal{E} and \mathcal{T} are respectively the energy and (conventional equilibrium) temperature of the reservoir: the reservoir always varies through quasi-equilibrium process. In such case, for all irreversible process where $dQ^{(1)} = 0$, the entropy variation of the closed total system is given as

$$\delta \bar{S}_{\text{tot}} = \sum_{n=2}^{\infty} \int_I \frac{dQ^{(n)}}{T_n} > 0, \quad (67)$$

where the inequality comes from (48). Thus, we expect $\sum_{n=2}^{\infty} \int_I \frac{dQ^{(n)}}{T_n} > 0$ in (64), and obtain the classical relation

$$\int_R \frac{dQ^{(1)}}{T_1} > \int_I \frac{dQ^{(1)}}{T_1} \quad (68)$$

for the case that the thermal reservoir is quasi-ideal as is described in (66).

VI. DERIVATION OF FLUCTUATION THEOREM

In the followings, to guarantee the precise microscopic dynamical time reversibility, we treat the combined system of the dynamical system H in (1) and its external environment system as a completely isolated Hamiltonian dynamical system, and write Hamiltonian \mathcal{H} as

$$\mathcal{H}(x) = H + V_{\text{int}} + H_{\text{ext}}, \quad (69)$$

where H_{ext} denotes the Hamiltonian of the external environment and V_{int} is the interaction potential between the system H and H_{ext} as previously introduced. The phase space Γ represents the total phase space defined by the canonical variables of H and H_{ext} , and $x \equiv (q_1, \dots, q_N, p_1, \dots, p_N)$ represent a point in this total phase space Γ .

Then, for the completely isolated system $\mathcal{H}(x)$, the macroscopically observed dynamics in Γ is given by the equations of motion (57) with the velocity field expressed as (56);

as previously argued, generally this velocity field is not incompressible. By the continuity equation (52) and (57), we obtain

$$\frac{d\tilde{\rho}(x, t)}{dt} = -\tilde{\rho}(x, t) \sum_i \frac{\partial \tilde{v}_i(x, t)}{\partial x_i}. \quad (70)$$

Let us consider an arbitrary trajectory $x(t')$ satisfying the equation of motion (57); let $x(t')$ satisfy $x(t_0) = x_0$ and $x(t) = x$. For the trajectory $x(t')$, from (70), we have

$$\tilde{\rho}(x, t) = \tilde{\rho}(x_0, t_0) e^{-\int_{t_0}^t \sum_i \frac{\partial \tilde{v}_i(t')}{\partial x_i} dt'}, \quad (71)$$

where $\frac{\partial \tilde{v}_i(t')}{\partial x_i} \equiv \frac{\partial \tilde{v}_i(x(t'), t')}{\partial x_i}$. In above equation, from the expression (58) for $\frac{d\tilde{S}}{dt}$, we can interpret the quantity $\sum_i \frac{\partial \tilde{v}_i(x, t)}{\partial x_i}$ as the entropy increment rate for a state x at t , and

$$\delta s \equiv \int_{t_0}^t \sum_i \frac{\partial \tilde{v}_i(t')}{\partial x_i} dt' \quad (72)$$

represents the entropy increment for the trajectory $x(t')$ during the time interval $[t_0, t]$.

For $x(t') \equiv (q(t'), p(t'))$, let us define

$$x^*(t') \equiv (q(t'), -p(t')). \quad (73)$$

Then, the time-reversed time series of $x(t')$ is given as

$$x^\dagger(t') \equiv x^*(t + t_0 - t'). \quad (74)$$

During the time interval $[t_0, t]$, the probability density to observe the time series $x(t')$ is

$$p(x(t'); [t_0, t]) = \tilde{\rho}(x_0, t_0). \quad (75)$$

On the other hand, *if the equations of motion (57) allows the time-reversed solution of the solution $x(t')$ during $[t_0, t]$, i.e., if $x^\dagger(t')$ can be a solution of (57) during $[t_0, t]$, the probability density to observe the time-reversed series $x^\dagger(t')$ during $[t_0, t]$ is*

$$p(x^\dagger(t'); [t_0, t]) = \tilde{\rho}(x^*(t), t_0). \quad (76)$$

Thus, using (71) and (72), we have

$$\frac{p(x^\dagger(t'); [t_0, t])}{p(x(t'); [t_0, t])} = \frac{\tilde{\rho}(x^*(t), t_0)}{\tilde{\rho}(x(t), t_0)} e^{-\delta s}. \quad (77)$$

Especially, if $x(t')$ starts and ends in a same stationary state as $\tilde{\rho}(y, t_0) = \tilde{\rho}(y, t) = \tilde{\rho}(y)$,

$$\frac{p(x^\dagger(t'); [t_0, t])}{p(x(t'); [t_0, t])} = \frac{\tilde{\rho}(x^*)}{\tilde{\rho}(x)} e^{-\delta s}, \quad (78)$$

where generally the stationary state $\tilde{\rho}(y)$ can be different from the equilibrium state expressed by $\tilde{\rho}(y) = \text{const}$ on an energy surface.⁹

In obtaining the results (77) and (78), we have assumed that the equations of motion (57) allows the time-reversed solution $x^\dagger(t')$ for an arbitrary given solution $x(t')$. However, as can be inferred from the expression (56) for $\tilde{v}_i(x, t)$, although the microscopic dynamics is always time-reversible, the macroscopic averaged dynamics (57) is generally not time-reversible. In the followings, we formulate the condition for the ensemble to guarantee the time-reversibility of the dynamics (57) for a given time interval $[t_0, t]$; then the condition will give the final form of the fluctuation theorem.

In order that the dynamics (57) is time-reversible during the time interval $[t_0, t]$, the equations of motion should be invariant under the transformation

$$(x, t') \rightarrow (x^*, t + t_0 - t'). \quad (79)$$

Replacing (x, t') with $(x^*, t + t_0 - t')$ in (57) and using (56), we obtain

$$\frac{dx_i^*(t')}{dt'} = - \int dx' \tilde{v}_i^o(x^*, x') \frac{\tilde{\rho}(x', t + t_0 - t')}{\tilde{\rho}(x^*, t + t_0 - t')}, \quad (80)$$

where, from (54),

$$\tilde{v}_i^o(x^*, x') = \frac{1}{\Delta t \Delta \Gamma} \int_{0, x^*}^{\Delta} ds dy \dot{x}_i(y) e^{-iL(y)s} \delta(y - x'). \quad (81)$$

In above expression, using $L(y^*) = -L(y)$ and (35), and noting that $\tilde{v}_i^o(x, x')$ a slow varying

⁹ For example, if the external environment system is constituted by two ideal thermal reservoirs with different temperatures with each other, where the ‘ideal’ means that they have infinite energy capacity, then the time length necessary to equilibrate the system $\mathcal{H}(x)$ becomes infinite, and $\tilde{\rho}(y)$ will be a non-equilibrium stationary state.

function for x and x' as $\tilde{\rho}$ in the sense of (12)¹⁰, we can write

$$\begin{aligned}
\tilde{v}_i^o(x^*, x') &= \frac{1}{\Delta t \Delta \Gamma} \int_{x^*, 0}^{\Delta} dy ds \dot{x}_i(y) e^{-iL(y)s} \delta(y - x') \\
&= \frac{1}{\Delta t \Delta \Gamma^2} \int_{x', x, 0}^{\Delta} dy' dy ds \dot{x}_i(y^*) e^{-iL(y^*)s} \delta(y^* - y') \\
&= \frac{1}{\Delta t \Delta \Gamma^2} \int_{x', x, 0}^{\Delta} dy' dy ds \dot{x}_i(y^*) e^{-iL(y)(s-\Delta t)} \delta(y - y'^*) \\
&= \frac{1}{\Delta t \Delta \Gamma^2} \int_{x', x, 0}^{\Delta} dy' dy ds \dot{x}_i(y^*) e^{-iL(y)s - iL(y'^*)\Delta t} \delta(y - y'^*) \\
&= \frac{1}{\Delta \Gamma} \int_{x'}^{\Delta} dy' e^{-iL(y'^*)\Delta t} \tilde{v}_i^{o*}(x, y'^*)
\end{aligned} \tag{82}$$

with the definition

$$\tilde{v}_i^{o*}(x, x') \equiv \frac{1}{\Delta t \Delta \Gamma} \int_{0, x}^{\Delta} ds dy \dot{x}_i(y^*) e^{-iL(y)s} \delta(y - x'). \tag{83}$$

Let us consider the velocity field obtained by replacing $\tilde{v}_i^o(x, x')$ in expression (53) with $\tilde{v}_i^{o*}(x, x')$, i.e.,

$$\tilde{v}_i^*(x, t) \equiv \int dx' \tilde{v}_i^{o*}(x, x'^*) \frac{\rho(x'^*, t)}{\tilde{\rho}(x, t)}. \tag{84}$$

Since $\tilde{v}_i^*(x, t)$ is different from $\tilde{v}_i(x, t)$ just in the sign of its components corresponding to $i \leq N$, the velocity field $\tilde{v}_i^*(x, t)$ is also slow varying function for t as $\tilde{v}_i(x, t)$ and $\tilde{\rho}(x, t)$. Thus, if we define $\mu_i(x, t) \equiv \tilde{\rho}(x, t) \tilde{v}_i^*(x, t)$, $\mu_i(x, t)$ varies slowly as

$$\mu_i(x, t + \Delta t) \approx \mu_i(x, t) + \frac{\partial \mu_i(x, t)}{\partial t} \Delta t. \tag{85}$$

Then, as the same as the process of obtaining (38) and (39), with the expression of μ_i given by (84) and Hermitian property of the operator $L(x, a)$, we have

$$\mu_i(x, t - \Delta t) = \int dx' \rho(x'^*, t) e^{-iL(x'^*)\Delta t} \tilde{v}_i^{o*}(x, x'^*) \tag{86}$$

and

$$\frac{\partial \mu_i(x, t)}{\partial t} = \int dx' \rho(x'^*, t) iL(x'^*) \tilde{v}_i^{o*}(x, x'^*). \tag{87}$$

Using (86) and (87), the condition (85) is written as

$$\int dx' \rho(x'^*, t) e^{-iL(x'^*)\Delta t} \tilde{v}_i^{o*}(x, x'^*) \approx \int dx' \rho(x'^*, t) [1 - iL(x'^*)\Delta t] \tilde{v}_i^{o*}(x, x'^*). \tag{88}$$

¹⁰ In obtaining the second line in (82), we have used $\int_{p-\Delta p}^p \approx \int_p^{p+\Delta p}$ for $\Delta x \equiv (\Delta q, \Delta p)$ as $\tilde{v}_i^o(x, x')$ is a slow varying function for x .

And, with the substitution $\rho(x'^*, t) = \tilde{\delta}(x' - y)$, we have the approximation

$$\frac{1}{\Delta\Gamma} \int_y^\Delta dx' e^{-iL(x'^*)\Delta t} \tilde{v}_i^{o*}(x, x'^*) \approx \tilde{v}_i^{o*}(x, y^*) - \Delta t \cdot \frac{i}{\Delta\Gamma} \int_y^\Delta dx' L(x'^*) \tilde{v}_i^{o*}(x, x'^*), \quad (89)$$

which is sufficient for the description of the slow variation of $\tilde{\rho}(x, t)$ as conditioned by (12). Then, applying (89) to (82), the expression of $\tilde{v}_i^o(x^*, x')$ in macroscopic realm can be written as $\tilde{v}_i^o(x^*, x') = \tilde{v}_i^{o*}(x, x'^*)$, i.e.,

$$\tilde{v}_i^o(x^*, x') = \frac{1}{\Delta t \Delta\Gamma} \int_{0,x}^\Delta ds dy \dot{x}_i(y^*) e^{-iL(y)s} \delta(y - x'^*). \quad (90)$$

Thus, substituting (90) to (80) and considering that $\dot{x}(y^*) = (-\dot{q}(y), \dot{p}(y))$ for $\dot{x}(y) = (\dot{q}(y), \dot{p}(y))$ and the definition (54), the transformed equations of motion (80) is identical with

$$\begin{aligned} \frac{dx_i(t')}{dt'} &= \int dx' \tilde{v}_i^o(x, x'^*) \frac{\tilde{\rho}(x', t + t_0 - t')}{\tilde{\rho}(x^*, t + t_0 - t')} \\ &= \int dx' \tilde{v}_i^o(x, x') \frac{\tilde{\rho}(x'^*, t + t_0 - t')}{\tilde{\rho}(x^*, t + t_0 - t')}. \end{aligned} \quad (91)$$

On the other hand, by (56) and (57), we have

$$\frac{dx_i(t')}{dt'} = \int dx' \tilde{v}_i^o(x, x') \frac{\tilde{\rho}(x', t')}{\tilde{\rho}(x, t')}. \quad (92)$$

From the condition that (91) should coincide with (92) for arbitrary $\tilde{v}_i^o(x, x')$, we obtain $\frac{\tilde{\rho}(x'^*, t+t_0-t')}{\tilde{\rho}(x', t')} = \frac{\tilde{\rho}(x^*, t+t_0-t')}{\tilde{\rho}(x, t')}$, which holds for arbitrary points x and x' ; thus, the condition for the time-reversibility of the macroscopic dynamics (57) is written as

$$\frac{\tilde{\rho}(x^*, t + t_0 - t')}{\tilde{\rho}(x, t')} = C(t'; t, t_0), \quad (93)$$

where $C(t'; t, t_0)$ is independent of x and a function of t' only, containing the parameter t and t_0 . Especially, in case of stationary state, the condition (93) is written as

$$\frac{\tilde{\rho}(x^*)}{\tilde{\rho}(x)} = C = \text{const}. \quad (94)$$

Also, if we substitute $t' = t$ in (93), we obtain

$$\frac{\tilde{\rho}(x^*, t_0)}{\tilde{\rho}(x, t)} = C(t, t_0) = \text{const}, \quad (95)$$

where the last equality $C(t, t_0) = \text{const}$ means that $C(t, t_0)$ is a fixed constant value for a given time interval $[t_0, t]$.

Finally, using the above conditions (94) and (95), the fluctuation theorem [3] follows from (77) and (78)

$$\frac{p(x^\dagger(t'); [t_0, t])}{p(x(t'); [t_0, t])} = Ce^{-\delta s}. \quad (96)$$

Thus, we have the conclusion that, for an arbitrary closed Hamiltonian dynamical system with chaotic and ergodic properties, if a trajectory $x(t)$ is observed in macroscopic measurement for arbitrary (equilibrium or non-equilibrium) thermodynamic process and there exists non-zero probability to observe its time-reversed trajectory $x^\dagger(t)$ in the same process, the fluctuation theorem (96) always hold.

VII. CONCLUDING REMARKS

In this paper, we have constructed the generalized nonequilibrium extension of the entropy theory given by Gibbs and Einstein [1, 2]. Also, based on the generalized entropy theory, we have derived the fluctuation theorem. The entropy increment is directly connected with the presupposition (as is represented by (7) and (9)) that there are fast chaotic and ergodic motions which cannot be described in deterministic way under the given macroscopic measurement system. In macroscopic observation, such fast complex motions behaves as an ensemble potential in phase space (giving the interaction between ensemble elements), and resultantly, the phase space volume is not conserved. The entropy increment arises only for the imperfect observer who experiences the loss of the deterministic dynamical information by measurement imperfection. In this respect, the emergence of the irreversible physical time is an intrinsic phenomena to occur only for the imperfect observer by that the observer constantly loses physical informations.

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